

# Performance of a Treatment Loop for Recycling Spent Rinse Waters

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## Introduction

This paper summarizes an evaluation of a treatment loop designed to upgrade the quality of spent rinse waters discharged from 10 wet benches located in the fab at Sandia's Microelectronics Development Laboratory (MDL). The goal of the treatment loop is to make these waters, presently being discharged to the fab's acid waste neutralization (AWN) station, suitable for recycling as feed water back into the fab's ultrapure water (UPW) plant. The MDL typically operates 2 shifts per day, 5 days per week. Without any treatment, the properties of the spent rinse waters now being collected have been shown to be compatible with recycling about 30% (50/168) of the time (weekends primarily, when fab is idling) which corresponds to about 12% of the present water discharged from the fab to the AWN. The primary goal of adding a treatment loop is to increase the percentage of recyclable water from these 10 wet benches to near 100%, increasing the percentage of total recyclable water to near 40% of the total present fab discharge to the AWN. A second goal is to demonstrate compatibility with recycling this treated spent rinse water to the present R/O product water tank, reducing both the present volume of R/O reject water and the present load on the R/O.

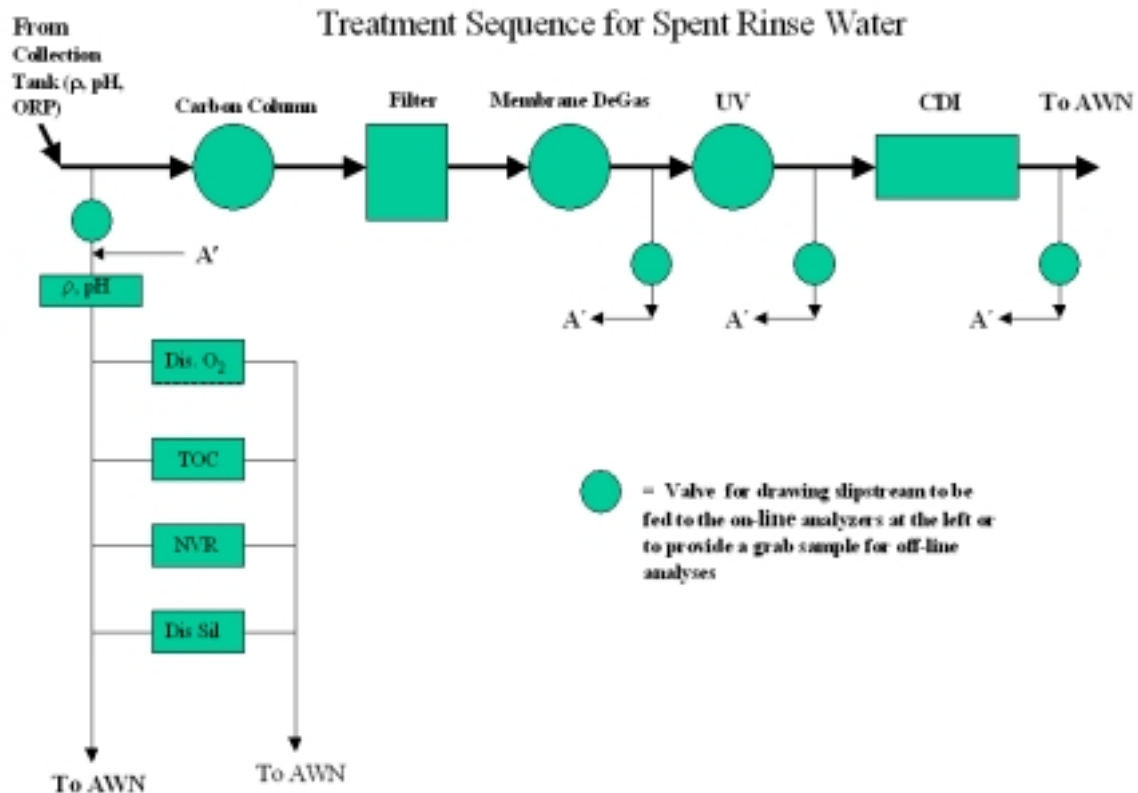
The approach taken to demonstrate achieving these goals is to compare all the common metrics of water quality for the treated spent rinse waters with those of the present R/O product water. Showing that the treated rinse water is equal or superior in quality to the water presently stored in the R/O tank by every metric all the time is assumed to be sufficient argument for proceeding with plans to incorporate recycling of these spent rinse waters back into MDL's R/O tank.

## Treatment Loop

Figure 1 shows the components of the initial treatment loop evaluated. Spent rinse water from the collection tank enters the treatment loop through a carbon column. The primary role of the carbon column is to protect the downstream CDI unit from oxidizing species that could degrade the resins. The next module is a filter to capture any carbon particles entrained in the water flow as well as any extraneous debris from the fab. A membrane degasifier then follows to remove oxygen and carbon dioxide absorbed from the open plenums that collect the rinse water in the fab. This unit is upstream of a 185 nm UV module inserted for bacteria control and potentially some TOC destruction. Finally, the

last module is an electrodeionization unit (labeled CDI in Fig 1., reflecting the manufacturer's trademark) for removal of ions.

All modules were sized for a flow rate of 5 gpm. The dark arrows in Fig. 1 show the path of the main 5 gpm flow through the treatment loop. At various nodes along this path, slipstreams are available for both on-line and off-line analyses, as indicated by the lighter weight lines in Fig. 1. Switching from one sampling node to another requires changing the plumbing manually. Most data were collected from the node downstream of the CDI which corresponds to the product water from the entire treatment loop.



**Figure 1. Schematic of the Initial Treatment Chain Evaluated**

Figure 1 also identifies the major on-line analyzers used in the evaluation:

- 1.) A dissolved oxygen analyzer-- Orbisphere Model 3660
- 2.) A Total Oxidizable Carbon analyzer -- Sievers Model 800 Turbo
- 3.) A Nonvolatile Residue Monitor -- PMS Liquitrack, 7700 Series
- 4.) A dissolved silica monitor -- Hach Model 5000

In-line sensors included cells for measuring resistivity, pH and oxidation-reduction potential (ORP). One of each of these in-line sensors is inside the collection tank. Resistivity and pH cells are also in the discharge line to the AWN and in the feed lines leading from the fab to the collection tank (not shown).

Six of these seven parameters made up the performance matrix used to compare the quality of CDI product water with that of R/O product water (ORP was omitted from the comparison.).

The following manufacturers lent the major control modules making up the treatment chain:

- 1.) The membrane degasifier (Liqui-Cel ) -- Celgard LLC, Charlotte, NC
- 2.) The UV reactor -- Trojan Technologies, London, Ontario
- 3.) The electrodeionization unit (CDI ) -- US Filter, Lowell, MA
- 4.) The carbon column -- US Filter, Albuquerque, NM

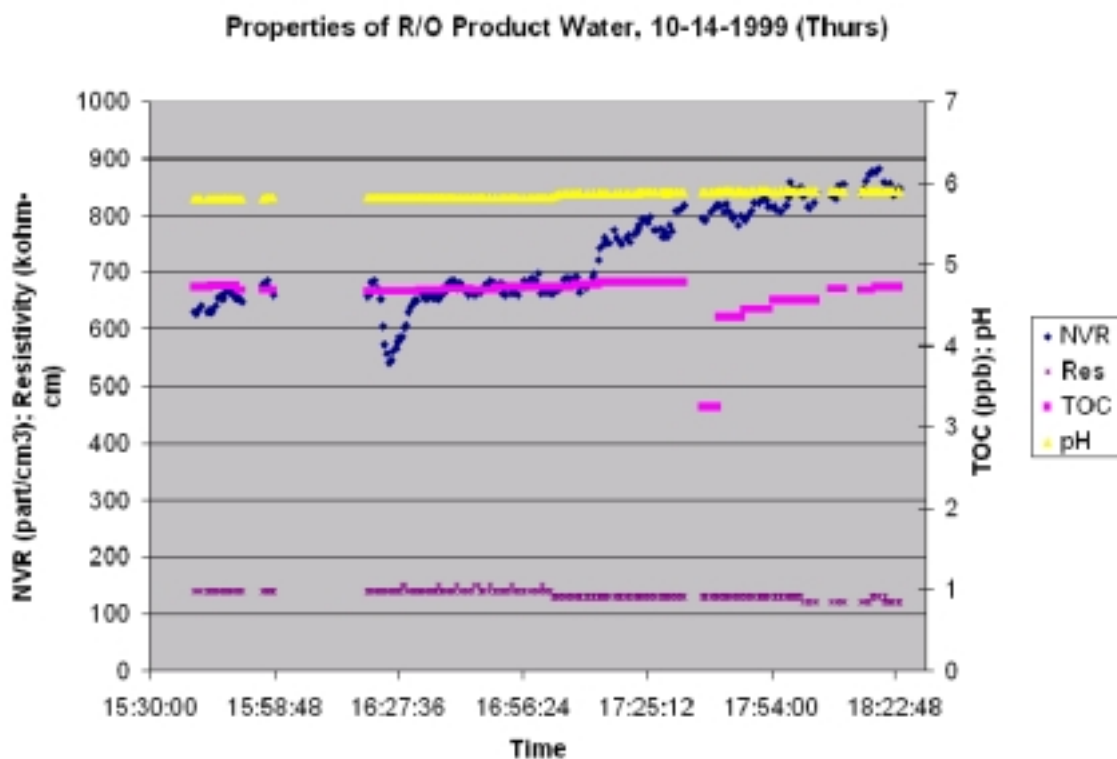
### Test Plan

The test plan consisted primarily of comparing CDI product water properties during fab operating hours with those of R/O product water, which remain essentially the same regardless of fab operating status.

### Properties of R/O Product Water

Figure 2 shows the typical range of R/O product water properties, which serve as the target values that, must be matched or exceeded in quality by the CDI product water. R/O product water is expected to be relatively stable over time, given the relative stability of the feed water provided to the UPW plant by the Air Force supplier. Thus, this brief 3-hour sampling of the R/O product water properties is assumed to be adequately representative of the MDL R/O water properties in general.

The concentration of TOC in ground water is much lower than that typically found in surface water and the combination of the carbon bed and the R/O used in the MDL UPW plant reduces the TOC in the R/O product water to the neighborhood of 4 - 5 ppb. The pH of this R/O product water is in the 5.8 - 6.0 range. Resistivity is between 100 and 200 kohm-cm, corresponding to conductivity in the 5 - 10  $\mu\text{S}/\text{cm}$  range. The nonvolatile residue (NVR) is high. It is plotted as particles/ $\text{cm}^3$  in Figure 2 rather than expressed as a relative concentration (ppb or ppm) because of the limitations in the range over which this particular NRM is calibrated. The calibration built into this analyzer spans the concentration range of 100 ppb to 20 ppm. (The particles/ $\text{cm}^3$  plotted in Figure 2 convert to about 3 ppm using this built-in calibration curve.) CDI product water and the MDL UPW contain much less NVR than 100 ppb. By reading the uncalibrated magnitude of the particles generated by evaporating the water droplets formed from an aspirated water sample, a measure directly related to NVR is obtained over the full range of values -- from UPW to the most contaminated of the waters evaluated in this test series.



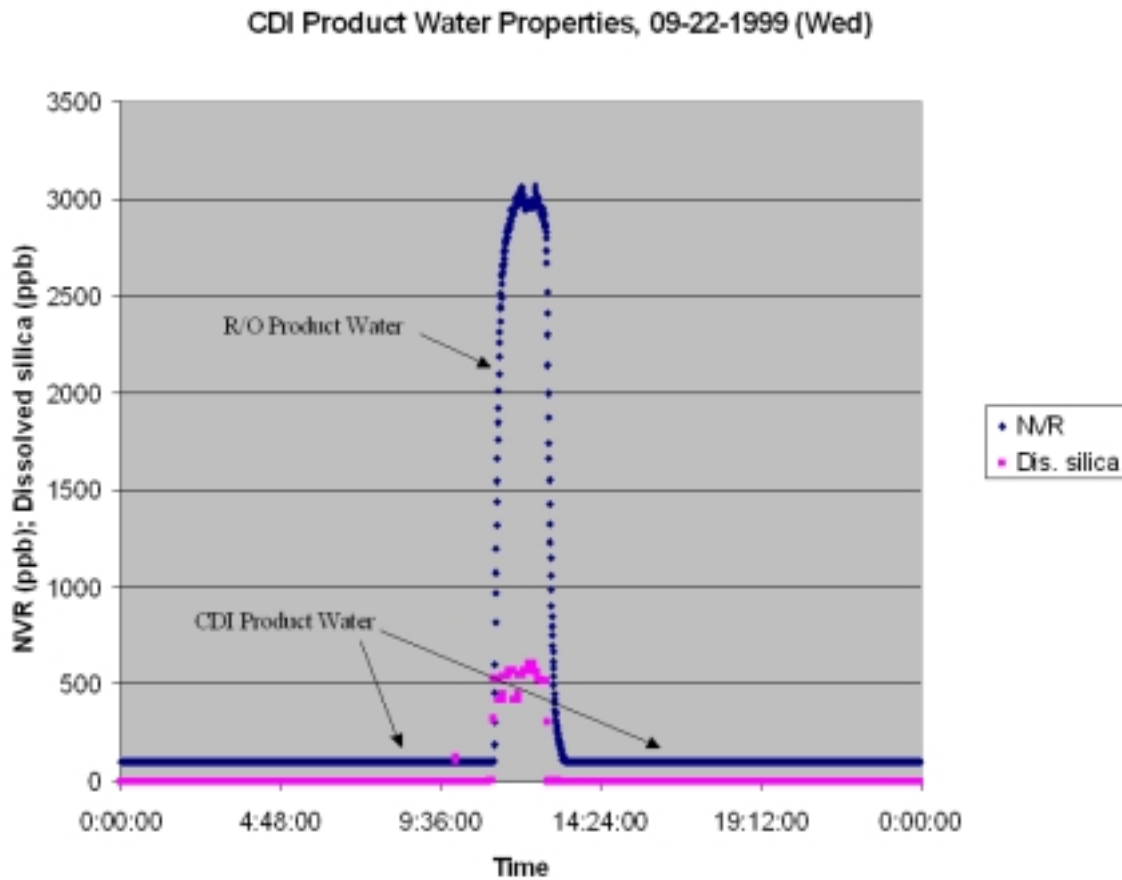
**Figure 2. Representative R/O Product Water Properties**

No data for dissolved oxygen are presented in that no degasifier was operating at the time these data were collected.

## **B. CDI Product Water Vs R/O Product Water**

### Dissolved Silica/NVR

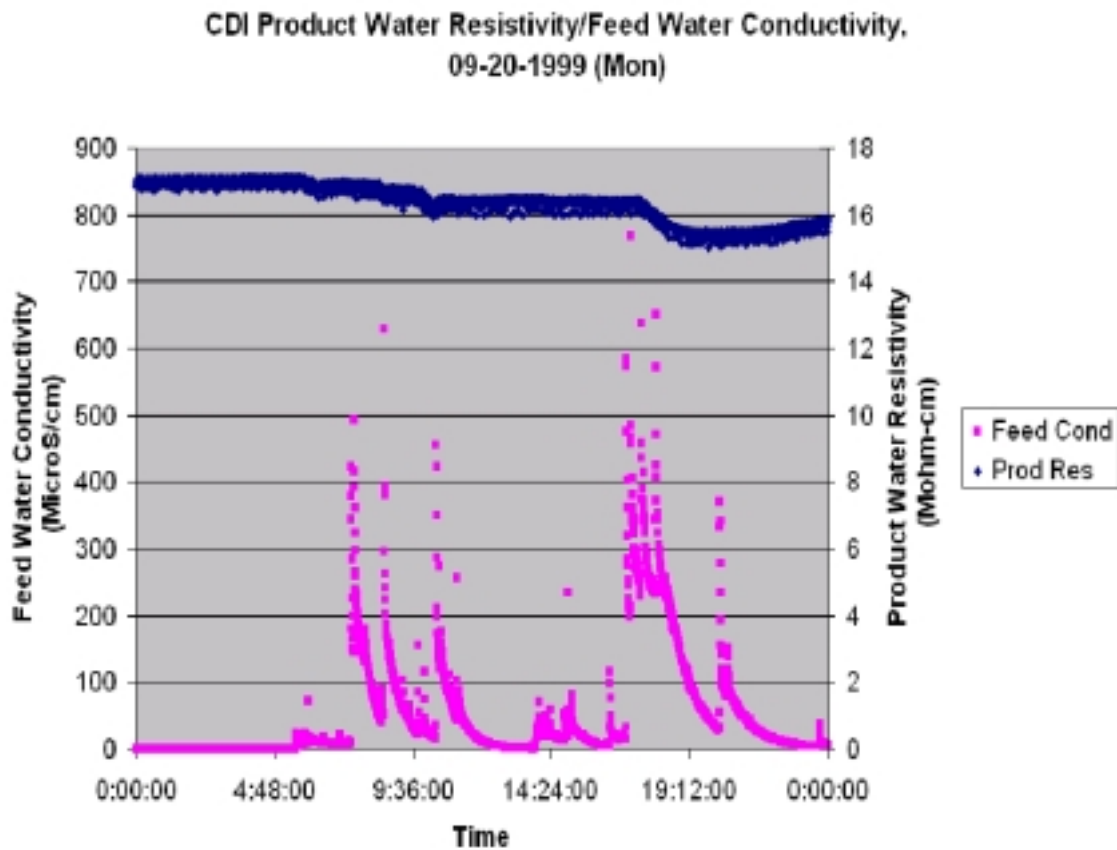
Independent, non-logged measurements of dissolved silica in R/O product water of the MDL's UPW system fall in the 500 - 1000 ppb range. Figure 3 compares typical concentrations of dissolved silica in R/O product water with that in CDI product water. It also shows the large jump in NVR brought about by switching from CDI product water to R/O product water. By these two metrics the quality of the CDI product water is far superior to that of R/O product water. NVR in Figure 3 is plotted in ppb unlike the units used in Figure 2. The NVR of the CDI product water is off-scale low in Figure 3 -- below 100 ppb.



**Figure 3. Comparison of NVR and Dissolved Silica in R/O Product Water with That in CDI Product Water**

#### Resistivity

Figure 2 shows that the resistivity of R/O product water falls in the 100 - 200 kohm-cm range. The resistivity of the CDI product water is typically an order of magnitude higher regardless of the resistivity of the spent rinse waters that make up the feed water to the CDI (Figure 4). In Figure 4, the units of conductivity for the feed water, given by the left-hand ordinate, are  $\mu\text{S}/\text{cm}$ ; CDI product resistivity, plotted on the right hand ordinate, is in Mohm-cm. The resistivity of the CDI product water remains well above 10 Mohm-cm even when the feed water resistivity exceeds 500  $\mu\text{S}/\text{cm}$ . And 10 Mohm-cm represents water quality far superior to that of R/O product water, as previously noted in Fig. 2. Thus by the resistivity metric, CDI product water also exceeds the water quality goal established at the beginning of the evaluation.



**Figure 4. Stability of CDI Product Water at Varying Feed Water Conductivities**

#### pH

The pH of the CDI product water is also very stable, remaining in the 6 - 7 range in spite of the large swings in pH that characterize the spent rinse waters discharged from the fab. Figure 5 illustrates the typical stability of the pH of the CDI product water and its insensitivity to variations in the feed water pH which swings from acidic to basic as one rinse bench then another dominates the properties of the rinse water. By this metric CDI product water is comparable in quality to R/O product water, again meeting the target performance requirement.

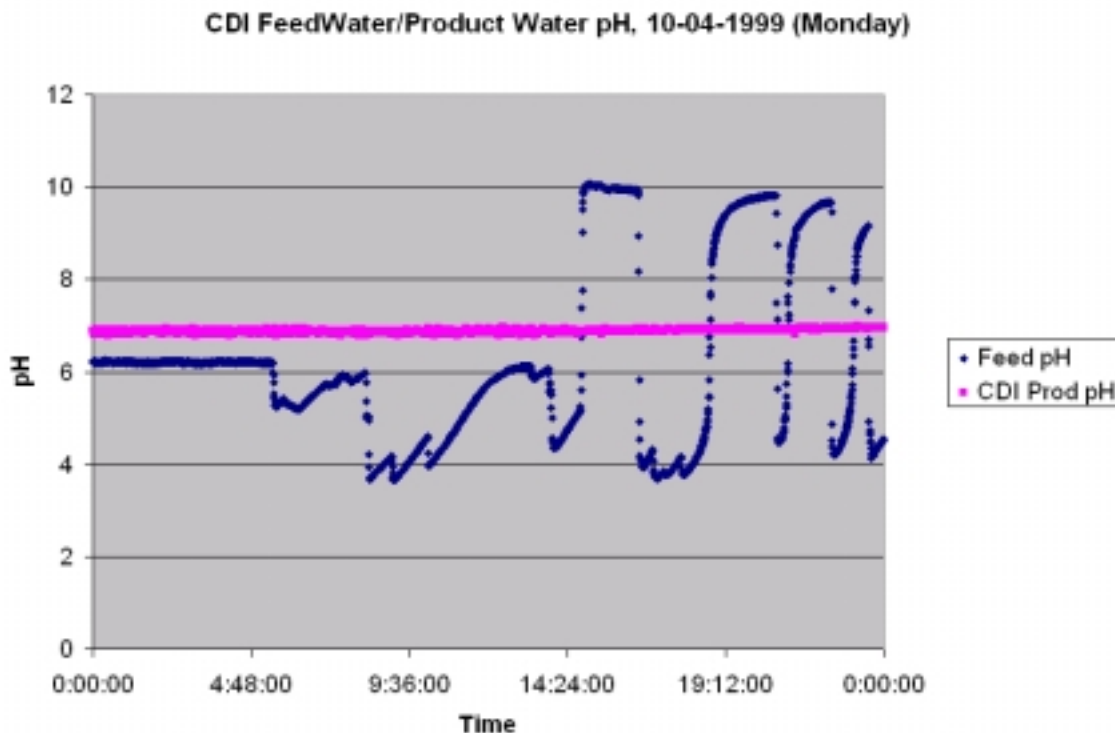
#### Dissolved Oxygen

With the present configuration of the MDL's UPW system, considerable uncertainty exists in assigning a reasonable, stable value of dissolved oxygen (DO) to R/O product water. Monitoring DO in the R/O product water without a degasifier module upstream of the R/O tank results in highly variable DO concentrations. However, there is little doubt that the feed water to the treatment loop is saturated with DO, the spent rinse waters from the wet benches being collected in plenums that are open to ambient fab air. And indeed the measured concentration of DO in the spent rinse water fed to the treatment loop is on

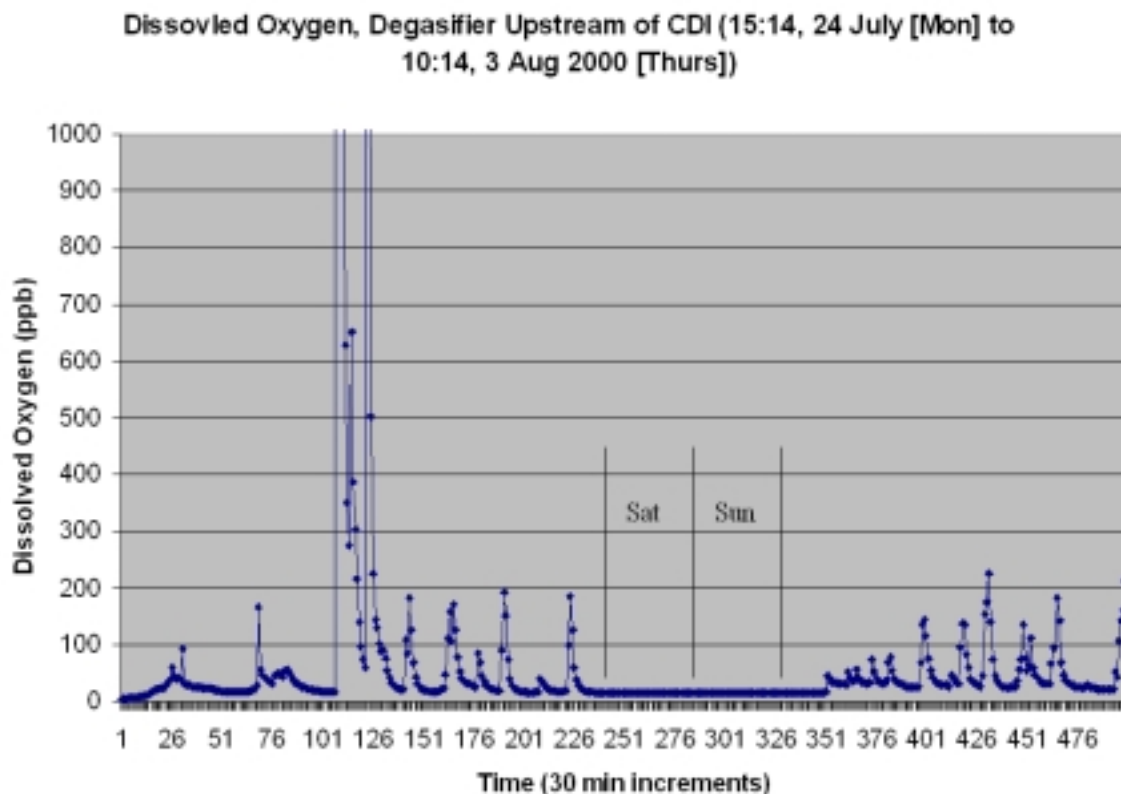
the order of 5.6 ppm or higher, regardless of the DO concentration in the R/O product water. The DO readings in these feed waters to the treatment loop remain relatively stable at the saturated concentrations, unlike the much lower DO readings in the R/O product water which exhibit significant fluctuations.

DO concentration in the CDI product water is also relatively stable at single digit ppb concentrations on the weekends when no fab processing is taking place. During the workweek, however, aperiodic excursions to DO concentrations, sometimes in excess of 1 ppm, occur, as illustrated in Fig. 6. These excursions are evidently caused by a trace contaminant, or a combination of contaminants, in the feed waters that perhaps temporarily wet some portion of the hydrophobic membrane of the degasifier. Such wetting would likely degrade the degasification capability of the wetted region so that a portion of the dissolved oxygen normally removed stays in the water.

The degradation is temporary and the membrane eventually recovers its normal degasification efficiency after the excursion. The data displayed in Fig. 6 were collected with the modules of the treatment loop in the order shown in Fig. 1, except that both the carbon column and the UV reactor have removed. If, in fact, a chemical species or combination of species causes the DO excursions, moving the degasifier downstream of the CDI would give the CDI a chance to remove the trouble-causing species. Figure 7 shows that this change in module order does in fact eliminate the excursions in product water DO concentration.



**Figure 5. CDI Product Water Stability with Respect to pH**

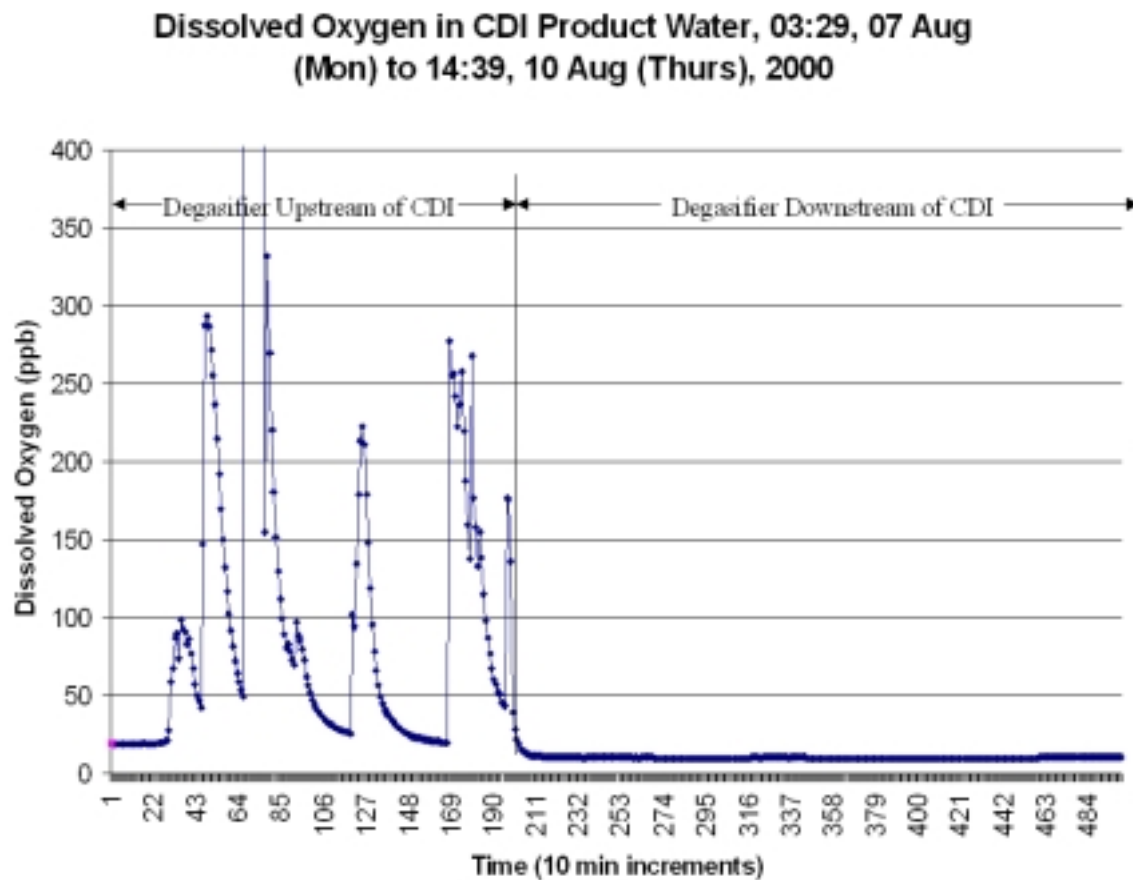


**Figure 6. The "Weekend" Effect in Dissolved Oxygen Concentration**

The treatment loop in Figure 7 consisted of only 3 modules (the filter, degasifier and CDI) rather than the 5 modules depicted in Figure 1. In the "degasifier upstream of CDI" configuration, the module order was: filter, degasifier, CDI. In the "degasifier downstream of CDI" configuration, the module order was filter, CDI, degasifier. Even in this latter configuration, however, minor excursions of small magnitude (10 - 20 ppb) and brief duration (~ 30 min), not evident on the right hand side of Fig. 7, sometimes appear. Thus, while the seriousness of the DO excursion problem has been significantly reduced, the problem has not completely vanished even in the degasifier downstream configuration.

In an attempt to identify the species causing the DO excursions, a brief series of inorganic chemical spikes, representative of fab wet processing, was carried out. To conduct these experiments, the feed water to the treatment loop was switched to just idle-flow UPW from several of the wet benches that were not in active use. A known volume of a selected spike chemical was dumped into one of these wet bench plenums so that the feed water to the treatment loop became idle-flow UPW spiked with just one, known chemical. No clear answer emerged from these spike tests. As shown in Figure 8, none of these single species spikes induced a significant excursion in DO concentration.



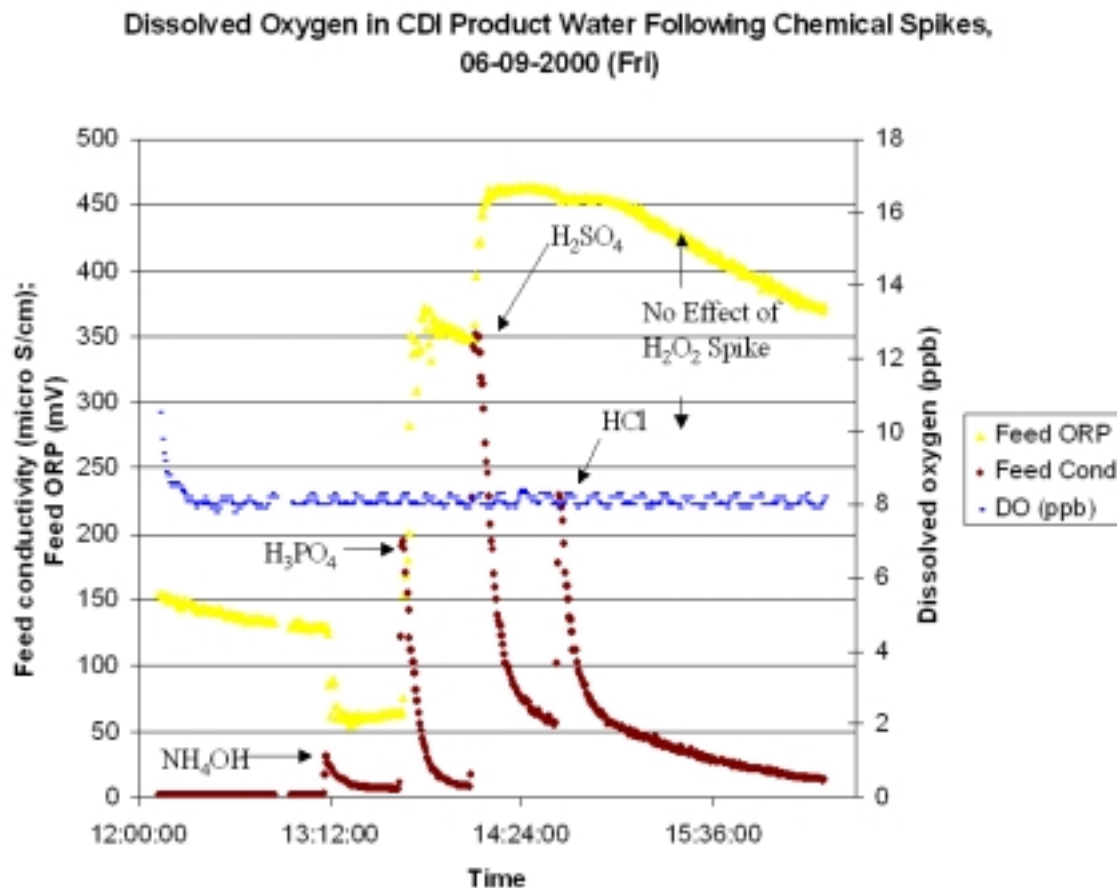


**Figure 7. Elimination of Excursions in DO Concentration with the Degasifier Downstream of the CDI**

Figure 8 further demonstrates the superior results resulting from the downstream location of the degasifier. To see the point being made here focus on the DO curve in the middle of the figure. The DO concentration remains at about 8 ppb throughout the 4 hour period during which these chemical spikes were added. The labels and arrows identify responses in the conductivity of the feed water that resulted from each chemical spike. Note that the DO concentration remained stable and unaffected by any of the chemical spikes (other product water properties [not shown] also remained fairly stable and little affected by the chemical spikes). While each of these spikes consisted of just one reagent, their lack of effect on the DO concentration in the product water led to the conclusion that the DO excursions reported earlier would not be a showstopper for recycling spent rinse waters to the R/O tank.

A remaining set of candidate experiments yet to be performed is one in which the degasifier is returned to its upstream location and a series of chemical spikes similar to those indicated in Figure 8 are repeated. This proposed experiment would be another

attempt to identify the chemical species or combination of species that produce the excursions in DO concentration that were observed with the degasifier upstream of the CDI unit. While the solution to this problem appears to be in hand, the cause of the problem is not understood. Neither the species triggering the degradation response nor the interaction by which it operates is known. This information could prove valuable in both the design and trouble shooting of membrane degasifiers in future UPW water systems.

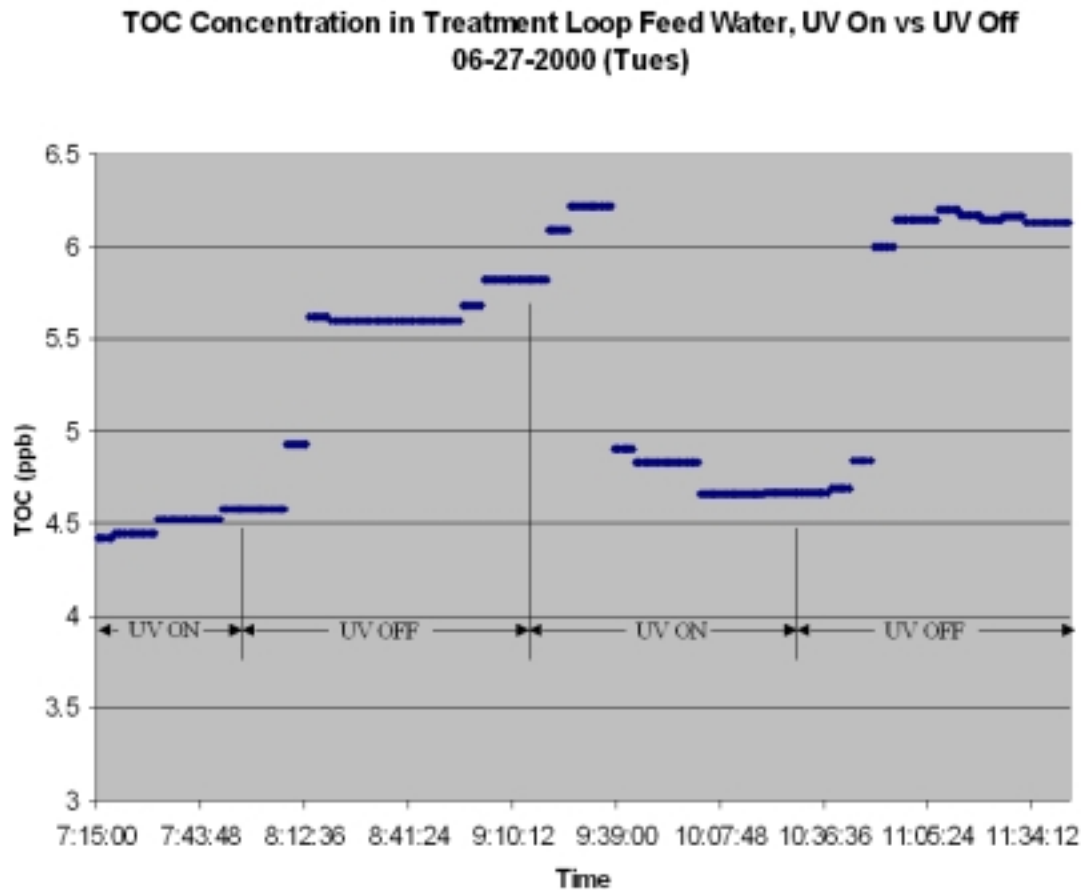


**Figure 8. Insensitivity of Downstream Degasifier to Single Species Spikes**

#### Total Oxidizable Carbon (TOC)

Typical concentrations of TOC in the R/O tank now range between 5 and 10 ppb; the TOC concentrations in the spent rinse waters to be recycled are mostly in the 10 - 15 ppb range with periodic excursions to the 50 - 100 ppb range or even higher. All TOC concentrations are measured with a Sievers 800T TOC analyzer operating in its normal mode (6 min cycle time).

The purpose of the UV reactor (Fig. 1) in the treatment loop is to destroy TOC by the same photochemical reactions used in TOC analyzers such as the Sievers 800. Figure 9 shows the effect of UV irradiation on the concentration of TOC in the feed water to the CDI unit of the treatment loop. The species dominating the TOC in the rinse water is generally not known so that the interaction illustrated in Figure 9 is not necessarily typical. However, these data do clearly show that turning the UV lamps On produces a reduction in TOC concentration.



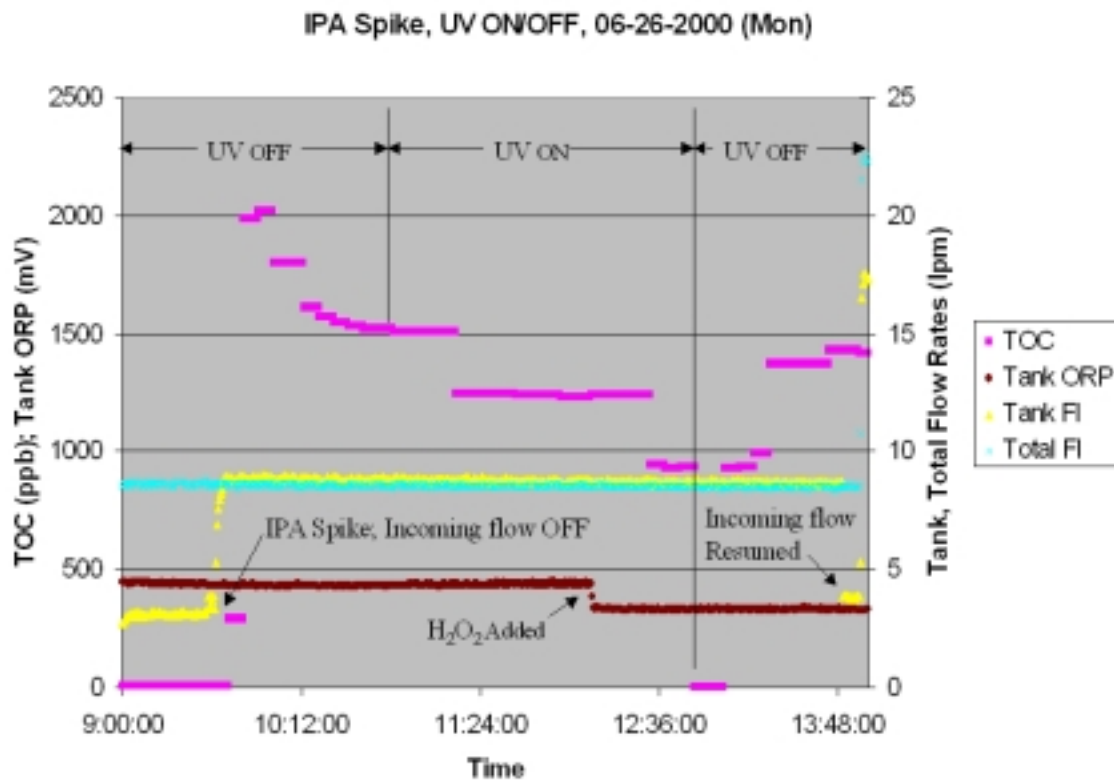
**Figure 9. Reduction of TOC Concentration in CDI Feed Water Attributable to UV Destruction**

Note that there is a lag time introduced by the non-zero response time of the TOC analyzer. With the UV ON, the CDI feed water contains about 4.5 ppb of TOC. When the UV lamps are turned OFF, the TOC of this same feed water climbs to about 6.2 ppb. These same concentrations are repeated as the state of the UV reactor is repeated.

The UV destruction of specific organic contaminants was investigated by a procedure modified somewhat from that of the DO studies:

1. The only feed water to the collection tank was idle UPW flow from 4 wet benches not in active use. Thus the collection tank water was UPW that had passed through a wet bench and been exposed to the atmosphere but had not been used to rinse any wafers or hardware.
2. With the collection tank full, a spike of known organic composition and liquid volume was added to one of the idle wet benches.
3. Immediately after step 2, all feed water to the collection tank was stopped. The collection tank thus became a source of constant TOC concentration for subsequent measurements.
4. TOC concentration could then be measured in the tank and at any node of interest in the treatment chain. Downstream of the CDI unit, as suggested by the UV reactor manufacturer, was the primary node for evaluating the impact of the UV reactor.

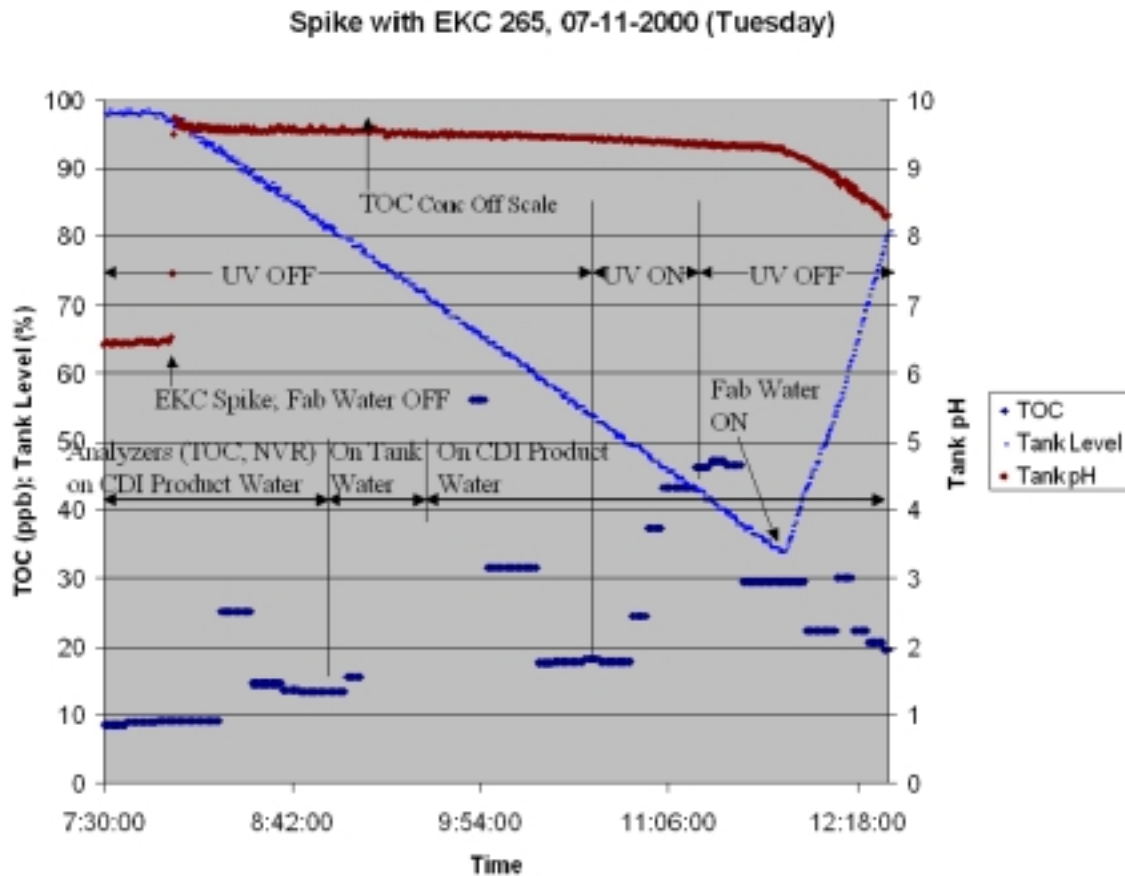
Figure 10 shows a typical TOC profile and sequence during these TOC spike tests.



**Figure 10. Spike Test Protocol Including Addition of Hydrogen Peroxide**

The IPA spike was introduced with the UV lamps OFF. After the spike stabilized at a concentration of about 1520 ppb, the UV lamps were turned ON, causing a reduction in TOC concentration to about 1240 ppb, an 18% decrease. A new wrinkle was introduced by adding hydrogen peroxide as indicated in the figure. This step further reduced the TOC concentration to about 936 ppb, an additional 25% reduction over the concentration measured with UV irradiation alone. When the UV lamps are once again turned OFF, the TOC concentration returns to near the TOC concentration measured in the tank following the initial IPA spike.

Several of the organics injected (TMAH, EKC 265 and Acetic acid) were efficiently removed by the CDI unit alone. This effect appears as a major reduction in TOC concentration between the tank value and that measured in the CDI product water with the UV lamps OFF. Turning the UV lamps ON in these instances slightly degraded the TOC destruction (the TOC concentration increased slightly when the UV lamps were turned ON). The organic species in these chemicals are evidently electrically charged and hence readily removable by the CDI. Turning the UV ON apparently converts some of the organic species to a less charged species which is not as easily removed by the CDI. In either UV state, however, the removal efficiency is high. Figure 11 is a plot of data showing this effect.



**Figure 11. TOC Destruction by the CDI Alone**

## Conclusions

For three of the six metrics of the evaluation (dissolved silica, nonvolatile residue and resistivity) the quality of CDI product water is clearly superior to that of R/O product water. For a fourth (pH), little difference exists -- the water is close to neutral in both product waters. Except for aperiodic spikes, TOC is just slightly higher in the CDI product water than in the R/O product water. Some TOC destruction by UV occurred with all the organic species of concern to the MDL Fab. Using higher intensity UV lamps in a reactor of longer residence time should reduce the TOC concentration in CDI product water to levels comparable to or less than those of R/O product water. The dissolved oxygen comparison is incomplete because of the uncontrolled DO concentrations observed in the R/O product water. However, moving the degasifier downstream of the CDI dramatically reduced the excursions initially observed with the Figure 1 configuration. The cause of these DO excursions was not identified but the answer to the observed problem is known.

Table 1 compares the properties of the various waters evaluated.

**Table 1. Water Quality Comparisons**

	MDL UPW	R/O Product Water	Spent Rinse Water*	CDI Product Water*
Resistivity (kohm-cm); [Conductivity (μSiemens/cm)]	~ 18000 [< 0.06]	100 - 200 [5 - 10]	2 - 200 [5 - 500]	> 10000 [< 0.1]
pH	6 - 7	6 - 8	2 - 10	6 - 7
Dissolved silica (ppb)	2 - 3	500 - 1000	3 -30	1 - 2
NVR (ppb)	1 - 2	>1000	>500	< 100
DO (ppb)	10 - 100	50 - 300	>5500	10 - 30
TOC (ppb)	1 - 2	5 - 10	5 - 200	10 - 100